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Advances in Environmental Research 7 (2003) 647–653

Advances in Environmental Research

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Hydrothermal decomposition and oxidation of the organic component of municipal and industrial waste products

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Abstract

The main objective of this study was to assess and compare the hydrothermal decomposition and oxidation trends of three waste types containing various quantities of the basic ingredients of biosolids; proteins, lipids, hydrocarbons and fibres. The three waste types were wastewater treatment sludge, wood waste and dairy waste. The wastes contained approximately 1.3–2% total solids (TS) and 20 400–26 700 mg/l chemical oxygen demand (COD). The experimental program consisted of hydrothermal treatment experiments conducted in a batch reaction vessel at temperatures in the range of 100–450 °C, oxidant (hydrogen peroxide) in the range of 0–150% of the COD, and reaction times of up to 60 min. The results confirmed that the waste composition, availability of oxidant, reaction temperature, and reaction time were the determining factors in terms of decomposition and oxidation effectiveness. The wood waste was the most difficult to decompose and thus required more aggressive treatment conditions to achieve results comparable to the other two waste types. The decomposition of the particulate organic matter and the maximum accumulation of dissolved organic decomposition by-products were achieved at 20% COD removal for the dairy waste, 40% COD removal for the sludge, and 60% TCOD removal for the wood waste. The data confirmed that the level of COD removal needed to achieve a desired level of accumulation of dissolved organic by-products could be achieved through balancing decomposition and oxidation using various combinations of the treatment conditions.

Keywords: Hydrothermal treatment; Oxidation; Hydrogen peroxide; Decomposition; Municipal sludge; Wood waste; Dairy waste

1. Introduction

The study presented in this paper is focused on processing the organic particulate matter of three types of waste streams using hydrothermal treatment. The general purpose of hydrothermal treatment is to disintegrate the particulate organic component of wastes converting the complex organic matter into simpler by products or harmless end products for discharge into the environment. The disintegration of organic solids is an important treatment objective in waste management. Hydrothermal treatment involves applying heat under pressure to achieve reaction in water. Hydrothermal treatment can be classified as subcritical or supercritical (Gloyna and Li, 1995; Shanableh, 1990). Subcritical treatment occurs at temperatures below 374 °C while supercritical treatment occurs at temperatures above 374 °C. Hydrothermal treatment can also be classified into two broad categories: (1) oxidative, involving the use of oxidants; and (2) non-oxidative, or does not involve the use of oxidants.

The organic component of wastewater sludge mostly exists in the particulate form. Only a small fraction of the organic component of fresh waste sludge exists in the dissolved form. The treatment of waste sludge at temperatures below 374 °C (subcritical temperatures)

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1093-0191/03/$ - see front matter
PII: S1093-0191(02)00042-4

results in the production of abundant quantities of dissolved organic matter from the sludge particles. The dissolved organic matter contains significant quantities of volatile fatty acids (VFAs), especially acetic acid, which remain in the liquid phase and are significantly removed at temperatures above 374 °C (Jomaa, 2001; Jomaa et al., 2000).

Dairy industries typically generate large quantities of wastes that are characterised by their high organic content (Nemererow and Dasgupta, 1991). The main components of dairy waste are proteins, fat and carbohydrates. The carbohydrates are almost entirely sugar (lactose). Upon thermal hydrolysis and partial oxidation, the dairy waste can potentially produce significant quantities of dissolved organic matter.

The manufactured products of the wood industry are wide and varied, and the industry generates large amounts of wastes, including solid and liquid wastes. Wood consists mainly of cellulose, hemicellulose and lignin (Sawyer et al., 1994). Cellulose and hemicellulose consist of sugar units. Hemicellulose and lignin decompose during the pulping process and are dissolved to basic sugar ingredients and other complex lignin products. Cellulose is typically more resistant to decomposition than hemicellulose.

Hydrothermal treatment offers an effective method for destroying organic particles. The destruction of particles proceeds through a variety of mechanisms including hydrolysis, oxidation, and gasification. Hydrolysis refers to splitting (breaking) up of the organic particles into smaller organic fragments in water. Biological solids for example are ruptured releasing their contents, including bound water, which hinders sludge de-watering. Hydrothermal decomposition also acts on the large organic molecules reducing them into smaller fragments, some of which dissolve in water.

Oxidation provides an ultimate method for the destruction of organic matter. Oxidation converts the fragmented organic matter into carbon dioxide, a gas, and water. The use of oxidant is critical in hydrothermal destruction of sludge solids. The lack of oxidant encourages char formation from sludge solids and simultaneously encourages gasification. Gasification also converts part of the organic content of sludge into volatile organic matter and the harmful carbon monoxide. If an oxidant is provided, the organic matter is converted to carbon dioxide and water. The extent of solids conversion to dissolved matter and degree of oxidation are dependent on the hydrothermal treatment conditions; temperature, reaction time and amount of oxidant supplied to satisfy the oxidation needs.

The main objective of this study was to assess and compare the hydrothermal decomposition and oxidation trends of three waste types containing various quantities of the basic ingredients of biosolids: proteins, lipids, hydrocarbons and fibres. These ingredients respond differently in terms of the ease or difficulty at which they decompose and oxidise. The three waste types contained various proportions of these ingredients and represented a range of organic ingredients found in waste matter of biological origin.

2. Materials and methods

A schematic of the batch reactor system used in this study is presented in Fig. 1 (Jomaa, 2001; Shanableh and Jomaa, 1998). The system consisted of a 30-ml stainless steel grade 316 (SS316) reaction tube (10 mm outside diameter×6.25 mm inside diameter×1000 mm long) equipped with a temperature control system (thermocouple, digital temperature display, and temperature regulator), and a pressure measurement system (pressure transducer and digital pressure display). The reactor assembly is connected to a shaker. The operation of the system is controlled using a computer which regulates the reaction time, temperature, mixing, and cooling time at the end of reaction. Cooling is achieved using a water spray. In running the system, the operator charges the tubular reactor with 10 or 20 ml of sludge and the desired amount of oxidant, H_2O_2, closes the reactor using the high pressure valves, and specifies the reaction temperature, duration, and cooling time. The operation of the system is achieved from behind a safety shield.

Waste treatment was evaluated under a variety of reaction conditions. The treatment parameters investigated were temperature, reaction time, and oxidant dose. The experimental program involved using three waste types, wastewater treatment sludge (secondary and a mixture of primary and secondary), dairy waste and wood waste (Table 1). For the mixed primary and secondary sludge, the treatment results were obtained using temperatures in the range of 150–450 °C, reaction times in the range of 0–60 min, and oxidant (H_2O_2) dose of 100% of the TCOD. For the secondary sludge and dairy and wood wastes, the treatment results were obtained using all of the possible 48 combinations of the following treatment conditions: (1) temperatures of 100, 150, 200 and 250 °C; (2) reaction times of 20, 40 and 60 min; and (3) oxidant (H_2O_2) dosages of 0, 50, 100 and 150% of the TCOD.

The analysis of samples collected for the purposes of evaluating the performance of the hydrothermal treatment were limited to chemical oxygen demand (COD), including total COD (TCOD) and soluble COD (SCOD), TS, and VS. The Hach methods were used for analysing COD and the other analytical procedures were conducted according to Standard Methods for the Examination of Water and Wastewater (APHA, 1995).

3. Results and discussion

Hydrothermal treatment of organic wastes is achieved in two major steps. The first step involves the transformation of the particulate organic component into smaller and soluble organic forms, and the second step involves the oxidation or gasification of the decomposed organic by-products. The formation of soluble organic matter is the result of breakdown of larger organic components of the sludge into smaller molecules. If the oxidising conditions are strong, the solubilised organic matter is oxidised and transformed into water and carbon dioxide mainly. The treatment conditions thus, can be chosen depending on whether complete or partial oxidation is required.

The destruction of the organic component of the mixed sludge tested in this study, characterised by the total chemical demand TCOD, as a result of hydrothermal oxidation is shown in Fig. 2. As temperature and residence time increased, TCOD decreased. More than 50% of the TCOD was removed in the first 10 min of reaction for all temperatures studied except at 150 °C. At 150 °C, it took approximately 60 min to achieve 50% TCOD removal. At the maximum oxidising conditions of 450 °C and 60 min, a maximum of 96% TCOD destruction was achieved.

The transformation of the soluble organic matter by hydrothermal treatment is affected by the rates of production through thermal decomposition of sludge solids and oxidation. The results for mixed sludge, as measured by the soluble chemical oxygen demand, are also shown in Fig. 2. As residence time increased, the SCOD increased to a maximum value then started to decrease at all temperatures studied. However, the SCOD reached a maximum value at shorter residence times as the temperature increased. When the temperature was 150 °C, the maximum SCOD reached 5820 mg/l at a residence time of 45 min. On the other hand, it took only 5 min to reach the maximum SCOD of 6400 mg/l when the temperature was 300 °C. The initial SCOD in the mixed sludge was 2680 mg/l and it increased by 250% to a value of 6600 mg/l when the temperature was 250 °C and a residence time of 10 min.

Table 1
Initial characteristics of sludge samples used in this study

Parameter	Mixed sludge	Secondary sludge	Wood waste	Dairy waste
COD, Total (mg/l)	21 000	21 300	26 700	20 400
COD, Soluble (mg/l)	2680	4070	1650	10 500
TS (mg/l)	19 900	21 690	17 744	13 440
VS (mg/l)	12 980	15 200	17 380	12 250

The removal of TCOD reflected the aggressiveness of hydrothermal treatment as defined by the oxidant dose, reaction time and reaction temperature (Fig. 3). The data in Fig. 3 indicate that the removal of TCOD varied in the range of 0–51% at 100 °C, 2–64% at 150 °C, 3–78% at 200 °C, and 31–85% at 250 °C. The data

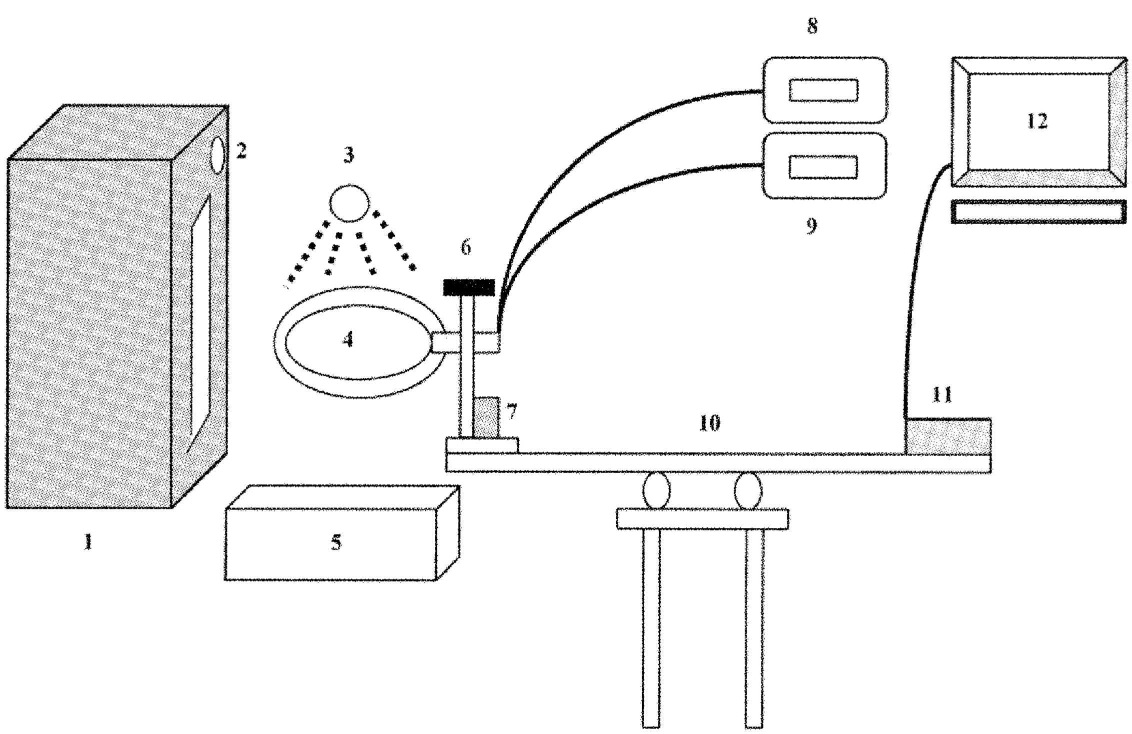

Fig. 1. Hydrothermal batch reactor apparatus.

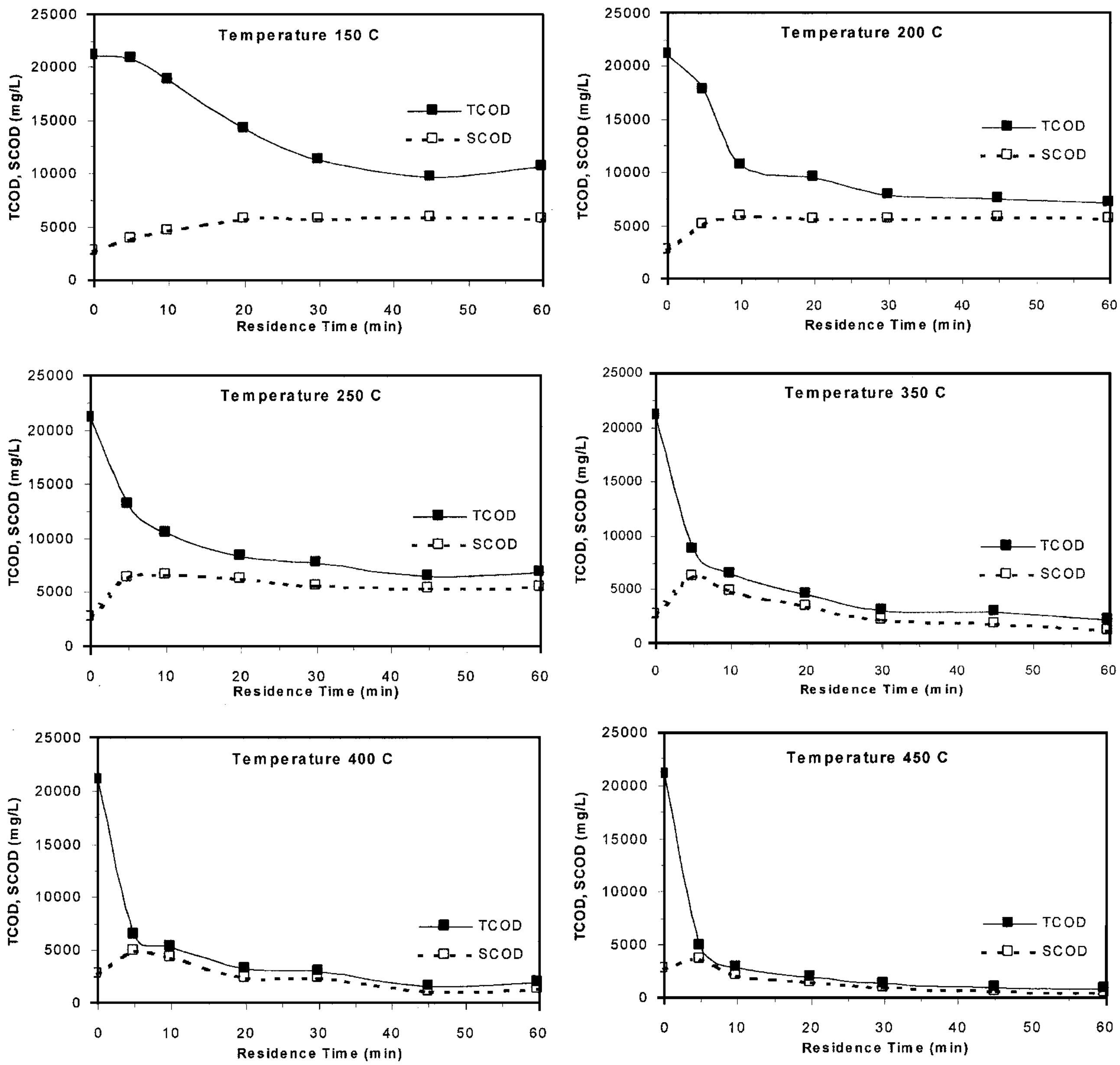

Fig. 2. Total COD and SCOD transformations in the mixed sludge. The results were obtained using an H_2O_2 dose of 100% of the TCOD.

clearly demonstrate the significant impact of oxidant use on the treatment results. At 100 °C for example, insignificant TCOD removal was achieved without oxidant while the use of oxidant resulted in TCOD removals of up to 51%. Also, without oxidant, the TCOD removal was limited to a maximum of 37% using the most aggressive treatment at 250 °C for 60 min. Using the oxidant (H_2O_2) in the range of 50–150% of the initial TCOD, the TCOD removal reached 60–85% at 250 °C. It should be noted that without the use of oxidant, the TCOD removal from the liquid phase could result from mechanisms such as gasification.

The data in Fig. 3 confirm that various combinations of reaction temperature, oxidant dosage and reaction time can result in the same TCOD removal. For example, approximately 40% TCOD removal from the sludge was achieved using either one of the following three treatment conditions: (1) 100 °C, 20 min and H_2O_2 dose of 150% of the TCOD; (2) 150 °C, 20 min and H_2O_2 dose of 100% of the TCOD; or (3) 200 °C, 40

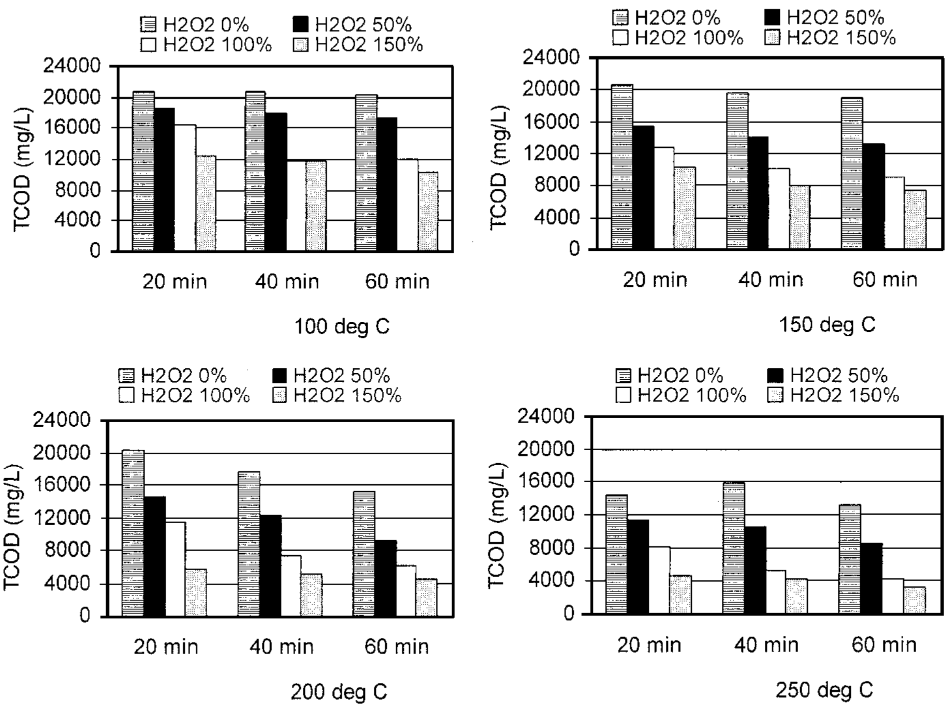

Fig. 3. Removal of TCOD from the secondary sludge using hydrothermal treatment.

min and H_2O_2 dose of 50% of the TCOD. The fact that the same level of treatment can be achieved using various combinations of the treatment conditions provides the design engineer with additional flexibility in terms of optimizing system design.

The data in Fig. 4 are presented normalized as a function of TCOD removal. The smooth trends established by the data confirm the validity of the normalization approach in terms of summarizing the data. The smooth trends also suggest that the treatment results can be achieved using various combinations of reaction temperature, oxidant dosage and reaction time. Vallejo (1996) also used normalization in presenting similar results and concluded that the production of volatile fatty acids from sludge and other organic feedstock subjected to hydrothermal treatment was dependent on the level of treatment, regardless of the reaction conditions.

The study confirmed that hydrothermal treatment was capable of reducing the organic content of the three waste types effectively. The COD removals in Fig. 4 were in the range of 1–85% for the sludge, 2–86% for the dairy waste and 8–86% for the wood waste. The treatment conditions used for the three waste types were similar and consisted of temperatures in the range of 100–250 °C, reaction times of 20–60 min, and oxidant (H_2O_2) dosages of 0–150% of the initial TCOD. The results suggest that the highest treatment efficiencies achieved using the most aggressive treatment conditions (250 °C, 60 min, H_2O_2 dose of 150% of the initial TCOD) were similar for the three waste types.

Of particular interest is the destruction of the organic suspended solids (particulate) component of the total solids. Direct measurement of the particulate (suspended) organic component of solids was not undertaken. Instead, an indirect measurement of the particulate COD (PCOD) was based on the difference between the total and soluble COD (TCOD–SCOD). The data in Fig. 4 show that the particulate organic component of the three waste types was effectively reduced to low levels through hydrothermal treatment.

The normalised data in Fig. 4a clearly show that the removal of PCOD associated with the secondary sludge particles was virtually complete when the TCOD removal exceeded approximately 40%. Once the destruction of the organic particles neared completion, the accumulation of SCOD peaked at approximately 11 000 mg/l and then started to decline.

The destruction of the particulate (suspended) organic component of wood waste proceeded faster than the destruction of TCOD due to the production and accumulation of dissolved organic matter during treatment. The normalised data in Fig. 4b show that the particulate COD was reduced to below approximately 2000 mg/l (92% removal) when the TCOD removal reached approximately 60–65%. As the suspended organic par-

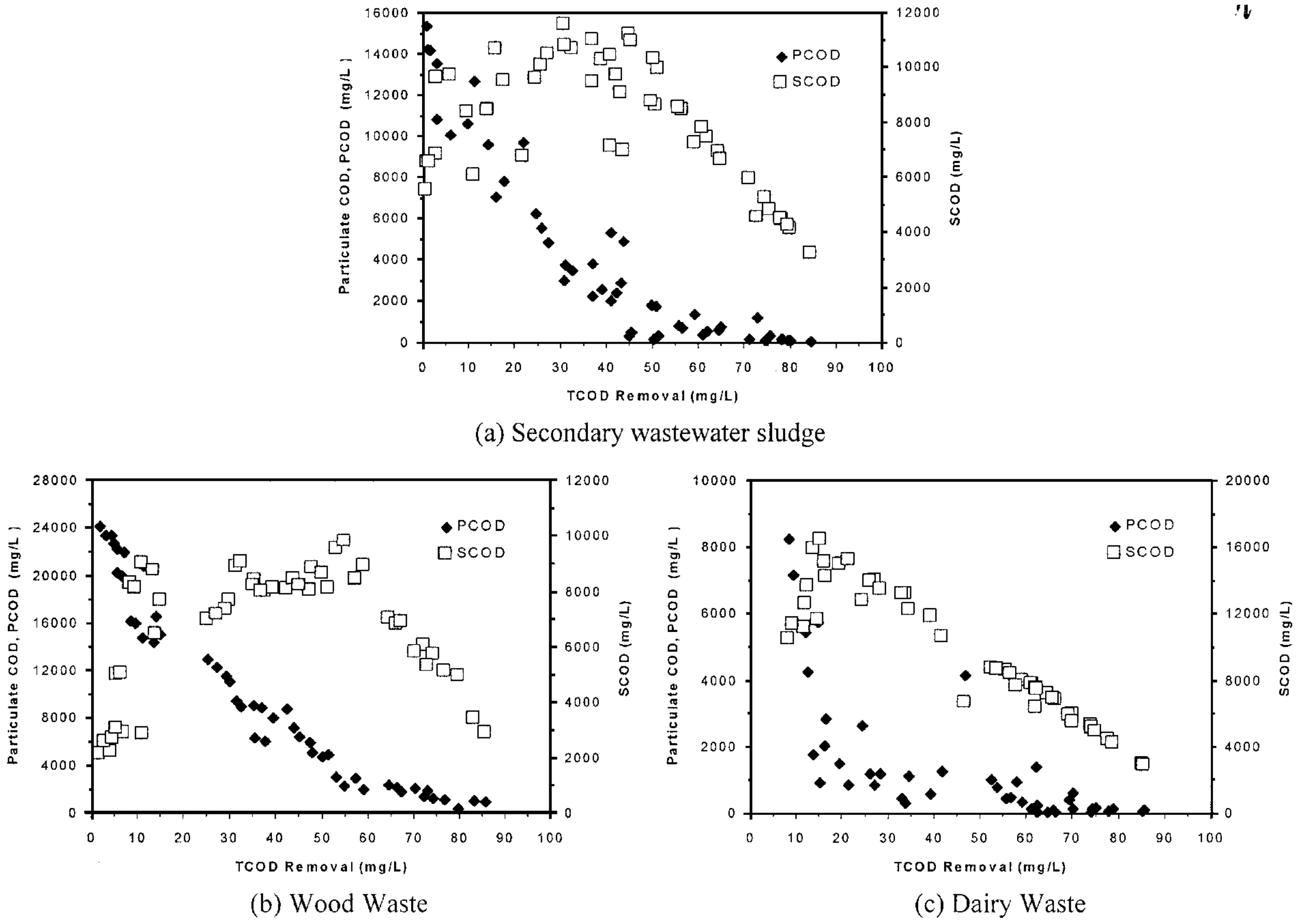

Fig. 4. Particulate COD and SCOD transformations as a result of hydrothermal treatment (TCOD in mg/l and TCOD removal in %). The results were obtained using temperatures in the range of 100–250 °C; reaction times of 20–60 min; and H_2O_2 dosages of 0–150% of the TCOD.

ticles disintegrated, the production and accumulation of SCOD continued to increase reaching a peak of approximately 8500 mg/l at approximately 90% particulate COD removal. The peak corresponded to a TCOD removal of approximately 60% TCOD removal.

The destruction of the particulate organic component of dairy waste occurred under the weaker treatment conditions used in this study. The data in Fig. 4c suggest that the removal of the particulate COD was virtually complete when the TCOD removal reached approximately 20%. The destruction of particulate COD proceeded faster than the destruction of TCOD due to the production and accumulation of dissolved organic matter during treatment. The normalised data in Fig. 4c shows that the particulate COD was reduced from an initial value of approximately 9900 mg/l to below approximately 1000 mg/l when the TCOD removal reached approximately 20%. As the suspended organic particles disintegrated, the production and accumulation of SCOD continued to increase (Fig. 4c) reaching a peak of approximately 16 000 mg/l at approximately 90% particulate COD removal. Following the removal of particulate COD, the original and produced SCOD declined in a linear form as a result of oxidation or other mechanisms.

Following the removal of particulate COD, the accumulated SCOD started to decline as a result of oxidation or other mechanisms. Based on a previous research study (Shanableh, 2000), the last significant SCOD component to be removed was acetic acid, which was considered to be thermally resistant. In general, the qualities of the SCOD, in terms of the organic components that make up SCOD, vary with the treatment levels achieved. The results suggested that the thermal decomposition and oxidation trends appeared to reflect the composition of the three waste types. The dairy particles appeared to be the easiest to decompose while the wood particles were the most difficult to decompose.

4. Conclusions

The decomposition of the organic particulate matter of the three waste types was accompanied by the production of dissolved organic matter. The maximum accumulation of soluble organic matter (as measured by SCOD) was achieved when the majority of the particulate organic matter was decomposed. The maximum SCOD concentrations and the majority of the particulate organic matter removals were achieved as the TCOD removal reached 20% for the dairy waste, 40% for the sludge and 60% for the wood waste. The maximum SCOD concentrations were approximately 11 000 mg/l for the sludge (52% of the initial TCOD), 8500 mg/l for the wood (32% of the TCOD), and 16 000 mg/l for the dairy waste (78% of the TCOD). The results confirmed that that the waste composition, availability of oxidant, reaction temperature, and reaction time were the determining factors in terms of decomposition and oxidation effectiveness.

Acknowledgments

The results presented in this study are part of a research project led by the principal investigator, Dr Abdallah Shanableh, and funded by various organisations including a grant from the Australian Research Council (ARC). The study was conducted at the Queensland University of Technology, Brisbane, Australia.

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